# SPECIATION OF NICKEL IN RESIDUAL OIL FLY-ASH BY XAFS SPECTROSCOPY

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## ABSTRACT

The US EPA has recently expressed concern about the possible presence of carcinogenic nickel subsulfides (*e.g.* $Ni_3S_2$, *etc.*) in fly-ash generated and released during combustion of residual oil for power generation. To examine the forms of nickel in residual oil fly-ash samples, we have used a combination of X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction, and a sequential extraction-anodic stripping voltammetry (ASV) technique. Differences were found in the nickel speciation between experimental (7 kW) and commercial (400 MW) combustion systems burning similar 0.85 wt% sulfur residual oils. Whereas almost all of the nickel was found to occur as nickel sulfate in the fly-ash from the experimental system, the fly-ash from the commercial system contained significant nickel in the form of a spinel phase, possibly $NiFe_2O_4$. No significant evidence was found for the occurrence of any nickel sulfides in any sample, suggesting the cancer risk from Ni in residual oil fly ash is greatly exaggerated.

## INTRODUCTION

The combustion of residual (No. 6) fuel oil for steam generation has the potential to release significant quantities of various metals, specifically vanadium, nickel, and chromium, and the semi-metal, arsenic, into the atmosphere [1]. Further, unlike fly-ash products from coal combustion, which contain abundant aluminosilicates that can react with and sequester trace metals in relatively unreactive glassy forms, fly-ash products from residual oil combustion usually do not contain significant quantities of aluminosilicates and the occurrence of these metals in residual-oil fly-ash is principally as oxides or sulfur compounds, either sulfates or sulfides. In particular, there is much concern about the inhalation risk associated with nickel because of the potential for formation of highly carcinogenic nickel subsulfides ($Ni_3S_2$, *etc.*) in the fly-ash or fine particulate matter released during residual oil combustion [1]. Some limited nickel speciation analyses from power plants burning residual oil have reported as much as 26% of the Ni present as nickel subsulfides. However, it is possible that such values arise because of limitations in the indirect method used for speciating the nickel, *viz.*, sequential extraction-anodic stripping voltammetry (ASV).

In this investigation, we have used three complementary methods to examine the nickel speciation in residual oil fly-ash samples produced in laboratory- and commercial utility-scale combustion. These methods are nickel X-ray absorption fine structure (XAFS) spectroscopy, X-ray diffraction (XRD) and the sequential extraction-ASV technique. In addition, samples were measured by XAFS spectroscopy before and after the first step in the sequential-extraction procedure for a more direct comparison with the ASV method.

## EXPERIMENTAL

### (i) Sample collection

Laboratory fly-ash samples were generated by combustion of a 0.86 wt% sulfur residual oil in a bench-scale down-fired 7 kW combustion unit [2] at an excess $O_2$ concentration of about 3 mol%. In this unit, a peak temperature of about 1500°C was achieved for about 0.5 s after which the gas-stream was cooled at a rate of 600°C/s before being sampled at a temperature of 300°C. Commercial fly-ash samples were obtained by isokinetic sampling from the stack of a 400 MW boiler using a modified EPA method 17 sampling-train assembly [3]. Samples were collected on two consecutive days: on the first day, a 0.80 wt% sulfur residual oil was burnt; on the second day, a 0.88 wt% S residual oil was burnt. The temperature of sampling was approximately 290°C. Further details of the sampling are given in more detail elsewhere [4].

(ii)    Sample analysis methods

Ni K-edge XAFS spectroscopy was carried out at either beam-line IV-3 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, CA, or at beam-line X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY. Similar experimental practice was carried out at both synchrotron sources. Ash samples were suspended in the monochromatic X-ray beam using ultra-thin polypropylene bags. Nickel XAFS spectra were collected from the ash samples in fluorescent mode using either a 13-germanium array detector [5] or a Lytle fluorescence detector [6], depending on the concentration of the nickel. XAFS spectra were typically collected at X-ray energies ranging from about 100 eV below to at least 600 eV above the nickel K absorption edge. A thin nickel metal foil was used as the primary calibration standard; where possible, the foil was run in an absorption experiment after the fluorescence experiment so that it provided a simultaneous calibration. The first major peak in the derivative of the absorption spectrum of the foil was assumed to define the position of the nickel absorption edge at 8,333 eV. In addition, XAFS spectra of a number of standard compounds of nickel were obtained in connection with this work. These spectra were obtained in absorption geometry from thin pellets using ionization detectors.

The XAFS data collected at the synchrotron were returned to the University of Kentucky for analysis. The data were analyzed in the usual fashion [7,8]: after calibration of the energy scale, the spectra were split into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions and each region was analyzed separately. The XANES region was used as a fingerprint for identification of the forms of occurrence of nickel in the fly-ash samples. The EXAFS region was mathematically manipulated in the usual manner [7,8] to yield the radial structure function (RSF), which is basically a one-dimensional representation of the local structure around the nickel in the material under investigation.

X-ray diffraction (XRD) was carried out on a Phillips XPert diffractometer system at the University of North Dakota using Cu $K_\alpha$ radiation, a step-size of $0.02°\ 2\theta$, and a time of 1 s/step. Diffraction patterns were collected over a range of $2\theta$ from 5 to 70°. Samples were ground in an agate mortar and pestle and mounted on quartz plate for the XRD analysis.

Sequential extraction-ASV analysis was performed at the University of Louisville. Although a five-step extraction sequence has been developed for determining nickel speciation in oil fly-ash [9], only the first step, designed to separate soluble nickel compounds from the residual oil fly-ash, was performed in this work. This step involved extracting the ash samples in a 1.0 M sodium acetate – 0.5 M acetic acid solution buffered at pH 5 in an 8 mL centrifuge tube and bubbled with nitrogen for 10 minutes. The capped tube was then sonicated in a water bath for 2 hours at 25°C and centrifuged at 10,000 rpm for 20 minutes. Nickel in the supernatant was quantified by ASV of nickel dimethylglyoxime collected on a hanging Hg drop electrode with a CH-620 electroanalytical system in square-wave voltammetry mode. Nickel concentrations were obtained by the standard additions method. The residue remaining in the centrifuge tube was repeatedly extracted until Ni was not detected in the supernatant. At this point it was assumed that all soluble nickel compounds had been removed from the fly-ash.

RESULTS AND DISCUSSION

(i)    XRD Analysis

X-ray diffraction analysis detected abundant amorphous components (glass, unburnt carbon) and anhydrite ($CaSO_4$) in all three fly-ash samples. In addition, the laboratory fly-ash sample contained gypsum ($CaSO_4.2H_2O$) and glauberite, ($Na_2Ca(SO_4)_2$), whereas the commercial fly ash sample collected on the first day of sampling contained hexahydrite ($MgSO_4.6H_2O$), periclase (MgO) and tentatively spinel, and that collected on the second day contained sodalite, ($(Na,Ca)_4$-$_8Al_6Si_6O_{24}(SO_4,Cl)_{1-2}$), and maghemite, ($\gamma$-$Fe_2O_3$). The magnesium phases are likely to have arisen from reaction and decomposition of brucite ($Mg(OH)_2$) that was added to the oil to mitigate formation of free $H_2SO_4$ in the boiler. No nickel phases were specifically identified.

(ii)    Acetate Extraction-ASV Analysis

The acetate extraction-ASV analysis divided the nickel into two fractions in each of the fly-ash samples: soluble nickel and insoluble nickel. For the laboratory fly-ash sample, 80% of the nickel was found to be present in soluble forms and the remainder in insoluble forms. For the two commercial fly-ash samples, significantly smaller fractions of the nickel were found to be present in soluble forms: for the Day 1 sample, 51%, and for Day 2 sample, 28%. In addition,

the total nickel concentration was found to be quite different between the laboratory and commercial fly-ash samples, viz., about 0.4 wt % and about 2.0 wt%, respectively.

(iii)   XAFS Spectroscopy

The nickel XANES and RSF spectra of the laboratory fly-ash are shown in Figure 1. The RSF exhibits one major peak at a phase-shift uncorrected distance, 1.61 Å, consistent with Ni-O distances, and the overall shape of the XANES spectrum is also consistent with bonding of the nickel to oxygen anions [10]. Based on comparison of the fly-ash XANES and RSF spectra with those of various nickel standard compounds [10], the best match was found to be a hydrated nickel sulfate (NiSO$_4$.xH$_2$O). The nickel XAFS data did not change significantly after the acetate extraction process, even though about 80% of the nickel was extracted. This indicates that the nickel is almost entirely present as nickel sulfate. Additionally and most significantly, there is no enhancement of any spectral features that can be attributed to nickel subsulfides, which, if they had been present to any significant extent in the fly-ash, should have been five times more prominent in the spectra of the extracted sample.

The corresponding spectra for the commercial fly-ash sample collected on the first day are shown in Figure 2, both before and after the acetate extraction. Quite similar spectra were
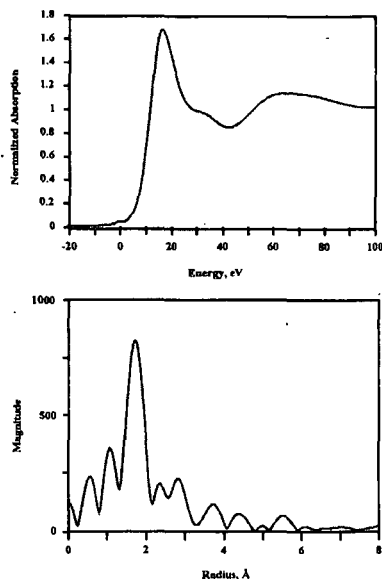
Figure 1:  Ni XANES (top) and RSF spectra (bottom) for fly-ash generated in the laboratory from combustion of residual (No. 6) oil. The spectra did not change significantly after the acetate extraction.
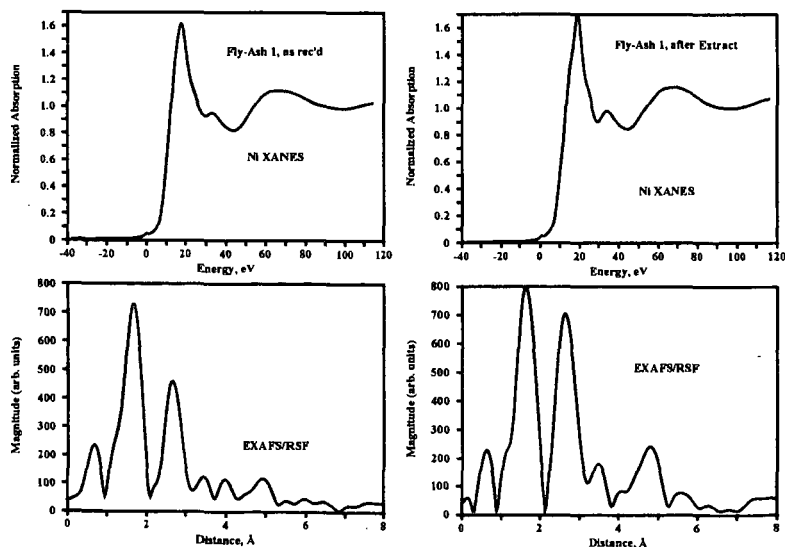
Figure 2: Ni XANES and RSF spectra for the residual oil fly-ash sample collected on day 1 at a commercial power plant, before (left) and after (right) extraction in a sodium acetate/acetic acid solution.

obtained from the fly-ash sample collected on the second day. As can be seen, there are significant differences in comparison with the spectra for the laboratory fly-ash sample and also between the spectra before and after the acetate extraction. In particular, the broad peak in the XANES spectrum at about 30-40 eV is more prominent and there is a second major peak in the

RSF spectrum at about 2.7 Å in the fly-ash samples from the commercial power plant. Both features become even more prominent after the acetate extraction.

Our first attempt at interpretation of the nickel XAFS data for the commercial fly-ash samples was in terms of a mixture of nickel sulfate ($NiSO_4$) and nickel oxide (NiO). Of the measured standard spectra that we had examined up to that point [10], only NiO had features in its XANES and RSF spectra that were consistent with the enhanced features shown in the corresponding spectra of the commercial fly-ash samples. However, the height ratio of the peaks at 1.6 and 2.7 Å, $A_{1.6}/A_{2.7}$, in the NiO RSF (Figure 3) is much different from that exhibited by the fly-ash and to explain the spectral data on the basis of a mixture of nickel sulfate and nickel oxide we would have to conclude that either (i) the acetate extraction removed only a very small fraction of the nickel as nickel sulfate, contrary to the results from the acetate extraction-ASV data, or (ii) that the reduction in the peak height ratio in the RSF was due to NiO of very small size. Neither of these explanations appeared very satisfactory.
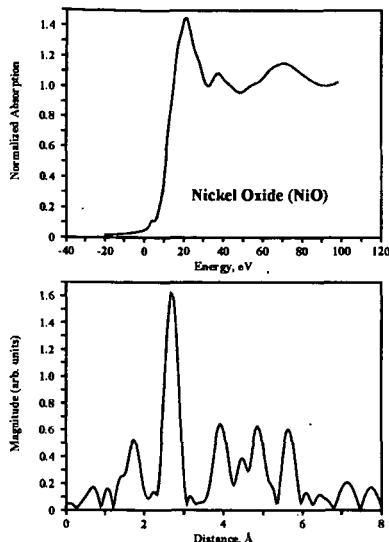


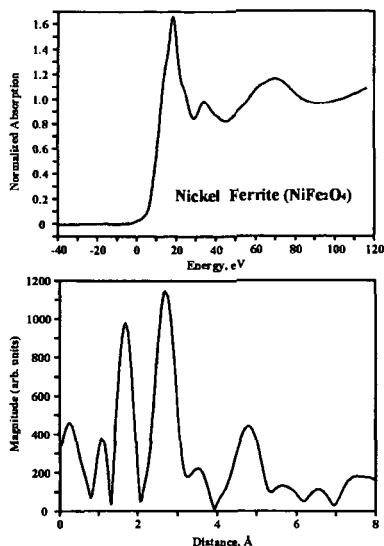Figure 3: Nickel XANES (top) and RSF (bottom) for
nickel oxide (NiO).

Figure 4: Nickel XANES (top) and RSF (bottom) for
synthetic nickel ferrite ($NiFe_2O_4$).

The XRD patterns for the fly-ash, however, had suggested the possible presence of a spinel phase and nickel is known to enter spinel compounds readily. Hence, the possibility was explored that nickel might be present as a spinel oxide in the fly-ash samples. A sample of the nickel spinel, nickel ferrite ($NiFe_2O_4$), was synthesized at high temperature at the University of North Dakota by reacting stoichiometric amounts of NiO and $\alpha$-$Fe_2O_3$ at 1600°C and 1400°C for 2 hours and 3 hours, respectively, in air. The purity of the spinel was confirmed using XRD; the measured cell parameter for this cubic material was 8.331 ± 0.006 Å in agreement with the value of 8.339 Å reported in the Powder Diffraction file No. 10-325 for $NiFe_2O_4$. The XAFS spectrum was then acquired in absorption geometry from a pressed pellet of the synthesized $NiFe_2O_4$ diluted in SOMAR mix. The Ni XANES and RSF spectra for the spinel are shown in Figure 4.

Comparison of the spectral data for $NiFe_2O_4$ with the data for the fly-ash samples provides a much better explanation than that for NiO. Not only is the ratio of the major peaks in the RSF of nickel ferrite much closer to that observed in the spectra of the extracted fly-ash samples, but the presence of a broad peak at about 4.8 Å in the RSF of nickel is also duplicated in the fly-ash spectra, especially those of the extracted samples. It is conceivable that the small differences in the height ratios of the major RSF peaks for the nickel ferrite standard and the extracted samples can be explained by the presence of aluminum or other light element substituting for the ferric iron in the spinel found in the commercial fly-ash. Hence, we do not now have to postulate that the acetate extraction incompletely removed the nickel sulfate, although that certainly remains a possibility, in light of the result obtained for the laboratory fly-ash. Regardless, the XAFS spectra of the extracted residues can be interpreted as arising from a substituted nickel-iron spinel as the predominant nickel-bearing phase.

Although less certain than for the laboratory fly-ash sample, there is no evidence from the XAFS data that there is any significant nickel sulfide species present in either of the commercial fly-ash

samples or their acetate extracts. Simulation of XANES spectra of hypothetical mixtures of the laboratory fly-ash and nickel sulfide (NiS) indicates that it should be possible to recognize a 5-10% occurrence of a nickel sulfide species in a fly-ash sample containing predominantly nickel sulfate species. The fact that spectral features attributable to nickel sulfides are not observed either for the fly-ash samples or their extraction residues indicates that such species are not significant and certainly less than 5% of the total nickel in the fly-ash.

## CONCLUSIONS

XAFS spectroscopy, supplemented by results from XRD and acetate extraction-ASV techniques, indicates that hydrated nickel sulfate is the major nickel compound present in laboratory-generated residual oil fly-ash samples, whereas nickel-containing spinel is a significant second component in commercial fly-ash samples obtained from combustion of residual oils of similar sulfur contents. As discussed elsewhere [4], it would appear that the magnesium hydroxide added to the commercial residual oil to prevent formation of free sulfuric acid in the boiler promotes the formation of nickel spinel by providing additional cation species that compete in reacting with the acidic sulfur species. In none of the fly-ash samples was there any evidence for the presence of nickel sulfides. This result suggests that the EPA's estimate of the nickel inhalation cancer risk from residual oil-fired utilities, which is based on the assumption that the nickel species emitted by such utilities have 50% of the cancer potency of nickel subsulfide [1], could be overestimated by as much as a factor of 10.

## ACKNOWLEDGEMENTS

## REFERENCES

[1]     Environmental Protection Agency, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress, Volume 1.* EPA Report EPA-453/R-98-004a, February 1998.

[2]     S. Benson, J. Pavlish, C. Zygarlicke, T. Erickson, K. Galbreath, G. Schelkoph, E. O'Leary, R. Timpe, C. Anderson, *Center for Air Toxic Metals Year 2 and 3 Final Technical Report—Section 3.0 Process Impacts on Trace Element Speciation.* Energy & Environmental Research Center Publication 98-EERC-03-03, April 1998, pp. 13-66.

[3]     Environmental Protection Agency, Emission Measurement Technical Information Center, Method 17, *Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method).* http://www.epa.gov/ttnemc01/promgate/m-17.pdf, September 1998.

[4]     K. C. Galbreath, D. L. Toman, C. J. Zygarlicke, F. E. Huggins, G. P. Huffman, J. L. Wong, *JAWMA*, submitted October 1999.

[5]     S. P. Cramer, O. Tench, N. Yocum, G. N. George, *Nucl. Instrum. Meth.*, **A266**, 586-591, (1988).

[6]     F. W. Lytle, R. B. Greegor, D. R. Sandstrom, E. C. Marques, J. Wong, C. L. Spiro, G. P. Huffman, F. E. Huggins, *Nucl. Instrum. Meth.*, **226**, 542-548, (1984).

[7]     P. A. Lee, P. H. Citrin, P. Eisenberger, B. M. Kincaid, *Rev. Mod. Phys.*, **53**, 769-808, (1981).

[8]     D. C. Koningsberger, R. Prins, *X-ray Absorption.* J. Wiley & Sons, New York, (1988).

[9]     J. L. Wong, J. Qian, C. H. Chen, *Anal. Chim. Acta*, **349**, 121-129, (1997).

[10]    K. C. Galbreath, D. L. Toman, C. J. Zygarlicke, F. E. Huggins, G. P. Huffman, J. L. Wong, *Energy & Fuels*, **12**, 818-822, (1998).